THE UNEQUAL HOST-PHASE DENSITY EFFECT IN ELECTRON PROBE DEFOCUSED BEAM ANALYSIS: AN EASILY CORRECTABLE PROBLEM

PAUL H. WARREN, Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095-1567, USA (current address), and Mineralogical Institute, University of Tokyo, Hongo, Tokyo 113, Japan

The defocused beam (or broad beam) technique of bulk-compositional analysis has a bad reputation, and deservedly so. Many literature analyses based on DBA are grossly inaccurate, typically showing erroneously high Al, and low Fe, Mg and Ti. The only widely cited correction methods for DBA [1,2] are completely inadequate, because they fail to account for the important effect of unequal density among host phases in the heterogeneous region excited by the defocused electron beam. Nazarov et al. [3] noted the need for density-based corrections, but unfortunately their recommendations have generally been ignored, perhaps mainly because their ultimate conclusion was, "for [rocks composed of] usual silicates . . . errors of DBA even with homogeneous correction are not significant." In fact, density corrections are essential for obtaining decent data, even for pure silicate rocks.

Conventional DBA correction procedures [1,2] assume that the DBA only needs to be corrected for normal ZAF effects, i.e., effects in the process by which each individual electron interacts with atoms in the target to produce characteristic (or noncharacteristic) X-rays that avoid absorption on their way out toward a spectrometer. It is probably true that ZAF corrections are significantly different for DBA than for a homogeneous target. But these methods overlook the more important effect of uneven density among the target phases. When a defocused beam is exactly half on plagioclase (ρ = 2.7 g/cm^3) and half on a dense mafic silicate (say 3.9 g/cm^3 olivine), equal numbers of electrons are striking plag and olivine. The resulting X-ray spectrum is, to a good first approximation, the average of spectra for analyses of the two pure phases. If only conventional ZAF corrections are applied, the DBA will yield a bulk composition that corresponds to 50 wt% plag, 50 wt% olivine. (I have confirmed this experimentally, by positioning the defocused beam halfway across flat plag/ilmenite, plag/pyroxene, and plag/Fe-metal interfaces.) But if the sample is truly a troctolite with 50 vol% plag and 50 vol% olivine, then its bulk composition is actually 59 wt% olivine + 41 wt% plag. Unless corrected for the unequal densities of the plag and olivine, the DBA will exaggerate the Al concentration by a factor of 50/41 = 1.22×, and the concentrations of Mg and Fe will be too low by nearly the same factor. I would regard systematic errors of such a magnitude as significant in almost any geochemical context.

The unequal host-phase density correction factor β_ρ can be described for each element *x* as

$$\beta_{\rho,x} = \sum_0^n \left(\frac{\rho_{phase}}{\rho_{bulk}} \right) \phi_{phase,x}$$

where $\phi_{phase,x}$ is the fractional contribution of the individual phase to the bulk-rock inventory of *x*. That is,

$$\phi_{phase,x} = \frac{V_{phase} \cdot C_{phase,x}}{\sum_0^n \left(V_{phase} \cdot C_{phase,x} \right)}$$

where V_{phase} is the fractional volume of the individual phase (i.e., mode %) and $C_{phase,x}$ is the average concentration (by weight) of *x* in the phase. Of course, if $V_{phase,}$ and $C_{phase,x}$ were exactly determined for all phases then there would be no need for DBA; the bulk composition could be calculated by the "modal recombination analysis" (MRA) technique [e.g., 4]. However, precise modes generally require some form of tedious point-counting. Also, a precise average phase composition may be difficult to determine if the phase is internally heterogeneous — and the DBA technique is only practical for samples that have fine- or medium-grained textures, which typically are associated with pronounced zonation in solid-solution minerals, such as pyroxene.

In general, for detectable elements in shallow-formed mafic igneous rocks, the most significant deviations of β_ρ from 1 are for Al, Na, K and to a lesser extent Ca, all of which tend to concentrate into phases significantly less dense than the bulk rock, plus Mg, Fe and especially Ti, which tend to concentrate into denser phases. Theoretical β_ρ values for a typical mare basalt are similar to the DBA correction factors derived for Al, Ca, Mg, Fe, and Ti by Dowty et al. [5] using a purely empirical method. These authors offered no theoretical explanation for the tendency for mare basalt DBA to yield obviously inaccurate results, although they speculated that the consistent need to

correct Al × 0.77 (as the most extreme example) is largely a consequence of systematic differential plucking of mafic silicates during the process of preparing thin sections. The correction factors of [5] have only been used for mare basalts, and for good reason. Note that β_ρ, although easily estimated, *is far from constant* for all sample types. In a mare basalt with 30% plag, Mg and Fe have β_ρ fairly close to 1, while Al, Na and K have β_ρ <<1. But in a 95%-plag anorthosite, where the bulk density is essentially the density of plag, Al, Na and K have β_ρ close to 1, while Mg, Fe and Ti have β_ρ >>1.

It is easy to show that satisfactory precision in the estimate of β_ρ requires only a very rough set of modal and phase-compositional data. Uncertainties that would ruin a pure modal recombination analysis can be tolerated as constraints for DBA. The mode only needs to be precise enough to give a rough indication of the mean (host-phase)/bulk density ratio for the element of interest. Consider, for example, the MRA results of [4] for Apollo 12 basalt 12072. The accuracy (or at least the representativeness) of this analysis has been questioned by Neal et al. [6], who argued that 12072 is not so feldspathic (Al-rich) as indicated by the MRA. Assuming (purely for the sake of illustration) the mode of [4] for 12072 should be modified by removal of 10 vol% plag and addition of 10 vol% pyroxene (maintaining the average px composition), then the MRA results should be modified by factors of 0.77-0.78 for Na and Al, and 1.11-1.13 for Mg and Fe. But the same modification to the mode only implies changes in the β_ρ for DBA by factors of 0.984-0.986 and 0.998-1.004, respectively. As another illustration (again, purely hypothetical), assuming that the mode of [4] was perfect, but their average px composition should be modified from $En_{34.6}Wo_{21.7}$ to $En_{41.0}Wo_{20.1}$, then the MRA results would be modified by factors of 1.088 for Fe, 1.027 for Ca, and 0.875 for Mg. But the same modification to the px composition only implies changes in the β_ρ for DBA by factors of 1.006, 1.001 and 1.002, respectively.

Examples of published DBA analyses that appear to be candidates for improvement by applying β_ρ corrections are so numerous, it almost seems unfair to single out a few of them for criticism. Two DBA analyses led [7] to discuss the microporphyritic vitrophyre ALH81001 as an unusually high-Al eucrite. However, the only phenocrysts in ALH81001 are pyroxene, not plag as would be expected if the parent melt was truly high-Al. Two conventional analyses show a normal Al content, and the same result can be obtained by modification of the original two DBA analyses using β_ρ corrections [8]. DBAs of "melt rock" portions of two angrites [9] show suspiciously high Al compared to conventional analyses of the same meteorites (which consist of "melt rock" plus 5-25 vol% virtually Al-free olivine). Many analyses of Luna 16 and 24 mare basalts are suspiciously Al-rich compared to conventional analyses.

In most cases, however, the accuracy of DBA is not easily gauged, because the technique (with its bad reputation) is seldom applied except to samples too small to permit conventional analyses. Moreover, one wonders, how many times have analysts quietly (but haphazardly) "corrected" DBA results by seeking to center the defocused beam on unusually mafic portions of the sample, and/or discarding a few embarrassingly high-Al analyses from the final data set? If this sounds far-fetched, consider the admission of [10] that "We have found it necessary in analyzing various rock samples to . . . exclude those analyses abnormally high in Al_2O_3 — thus introducing operator bias."

The DBA technique is potentially accurate and precise enough to warrant far more extensive application, including for many purposes (e.g., preliminary petrologic classification) analysis of large rocks. But without β_ρ corrections, DBA results will practically always contain serious errors. In future, practitioners of DBA should be exhorted to always apply β_ρ corrections, or at least to indicate unambiguously whether or not a set of DBA data have been corrected for the unequal host-phase density effect.

References: [1] Albee A. L. et al. (1977) *Lunar Sci.* **VIII**, 7-9. [2] Bower J. F. et al. (1977) In *Abstracts, 8th Int. Cong. X-ray Optics and Microanalysis*, p. 182-184. [3] Nazarov M. A. et al. (1982) *LPS* **XIII**, 582-583. [4] Beaty D. W. et al. (1979) *PLPSC* **10**, 115-139. [5] Dowty E. et al. (1973) *PLSC* **4**, 423-444. [6] Neal C. R. et al. (1994) *Meteoritics* **29**, 334-348. [7] Delaney J. S. et al. (1984) *LPS* **XV**, 212-213. [8] Warren P. H. et al. (1996) In *Workshop on Evolution of Igneous Asteroids* (eds. D. W. Mittlefehldt & J. J. Papike), p. 35-36. [9] Prinz M. & Weisberg M. K. (1995) *Antarct. Meteor.* **XX**, 207-210. [10] Albee A. L. et al. (1980) In *Eighth Int. Cong. X-ray Optics and Microanalysis*, p. 526-537.